Geochemical Mechanisms of Serpentine and Olivine Carbonation

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Introduction

Nature converts carbon dioxide (CO_2) into solids both at Earth's surface and in geological environments. The resulting carbonates (primarily calcium- and magnesium-based) store CO_2 in a stable, benign, and immobile form at the Earth's surface.

In 1995, Los Alamos scientists (Lackner and coworkers) proposed exploiting this process in an engineered solution for large-scale sequestration using magnesium derived from silicate rocks such as serpentinites (Fig. 1). This process is an intriguing advanced storage option with many advantages, but many scientific challenges remain.

The primary challenge for CO_2 mineralization is to determine a process that is viable: one that is sufficiently rapid to meet storage needs and cost competitive with respect to other options.

Fig. 1. Serpentinite deposit near Idria (CA) showing silica-carbonate ridge formed at elevated P and T. Magnesium carbonate is also actively forming via weathering in the soil. Serpentinite belts exist along both the coasts.

Fig. 2. Capacity increases along with technological challenges as you move through the land-based options for CO_2 storage, from terrestrial to geologic to mineralization. Mineralization capacity is sufficient for all conventaional fossil reserves, but feasibility depends on the rate at which carbonate minerals can be formed.
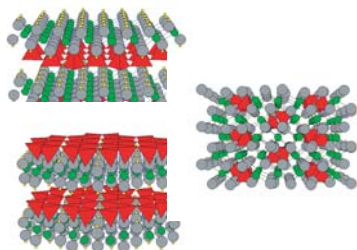

Fig. 3. Structure of the serpentine mineral lizardite (left) and olivine (right), showing octahedrally coordinated magnesium atoms (green) bonded to tetrahedral silica (red). Unlike olivine's isolated silica tetrahedra, those in lizardite are polymerized into sheets making them more resistant to dissolution. (Oxygen=gray; hydrogen=yellow)
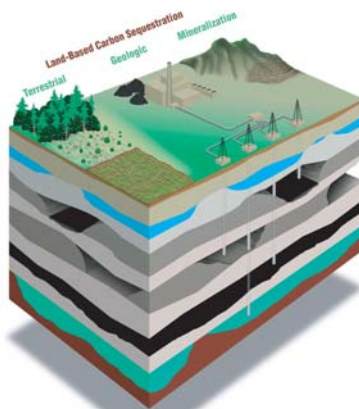
Several processes for the conversion of Mg-silicate to Mg-carbonate have been considered, but current efforts focus on carbonation in an aqueous medium, in which the magnesium is removed from the silicate by dissolution and subsequently precipitates as a carbonate (Fig. 4).
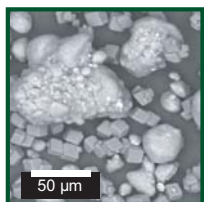

Fig. 4 Conceptual geochemical model of the aqueous conversion process. Supercritical CO_2 dissolves into the aqueous medium (1) and reacts with magnesium released by the dissolution of serpentine/olivine (2) to precipitate a magnesium carbonate (3). The scanning electron microscope image at the right shows solids recovered from a carbonation run: rhombic magnesite crystals precipitated from the solution following partial dissolution of the rounded serpentine grains.

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Is CO_2 mineralization possible in an engineered process?

Yes. Theoretically, magnesium carbonates are favored thermodynamically over magnesium silicates in the presence of CO_2 and water, at appropriate temperatures and pressures (Fig. 5).
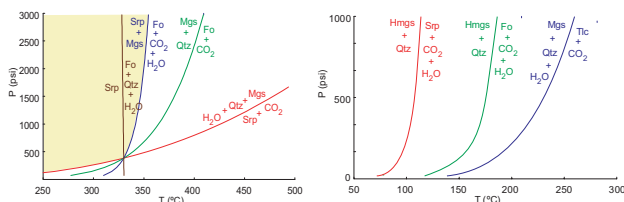

Fig. 5 Equilibrium relationships calculated for the solid phases in the system MgO-SiO_2-H_2O-CO_2. (Srp=serpentine; Fo=forsterite olivine; Mgs=magnesite; Qtz=quartz; Tlc=talc; Hmgs=hydromagnesite) The carbonation region is shown in yellow, bounded by magnesite thermal stability. In general, the optimum carbonation region lies below ~325 °C, but metastable and trace phases can limit the reaction to temperatures below 200 °C or even lower.

Yes. Experimental verification of the carbonation of magnesium silicates (both olivine and the more common serpentine minerals) can be achieved with rates that are sufficient for an industrial-scale sequestration process.

But... Significant conversion rates and efficiencies have only been achieved using either non-economic solution chemistries (e.g., drastic pH swings using HCl and NaOH; Carey et al., unpub.) or non-economic pre-treatment of the material (e.g., via heating or grinding; Fig. 6).
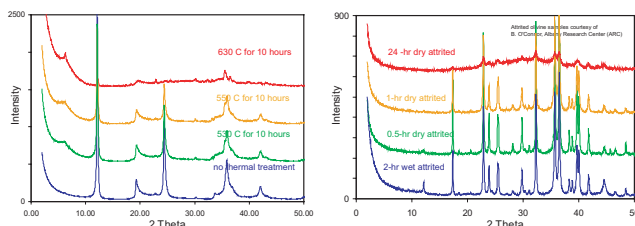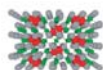

Fig. 6 X-ray diffraction patterns of serpentine (left) and olivine (right) following thermal pre-treatment and intense mechanical pre-treatment, respectively. In each case, the sample represented by the red diffraction pattern shows significant structural degradation, which correlates with high carbonation rates, as shown by Los Alamos (serpentine) and Albany Research Center (olivine; O'Connor and coworkers).
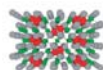
Is it viable? Neither of the pre-treatment methods (thermal or mechanical) appear to be viable as part of a process for CO_2 mineralization, due to the costs from energy penalties. Nor is an intense acid-base process viable, due to the cost of consumables.

A viable process for CO_2 mineralization must achieve sufficient carbonation rates with low energy penalties and with minimum consumables.

To identify a viable process, it is necessary to determine what controls the carbonation rate and how the rate can be enhanced. Both the dissolution of the silicate and precipitation of the carbonate may limit the rate of carbonation (Fig. 4). The kinetics of these steps are not well understood so are the focus of our geochemical research.

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What is the rate
of olivine carbonation?

The first step in aqueous carbonation is dissolution. Dissolution of Mg-rich olivine forsterite (Mg_2SiO_4) has been studied extensively at low temperature in aqueous geological fluids (e.g., Pokrovsky and Schott, 2000).

We have developed a geochemical model to understand the role of dissolution during olivine carbonation (Figs. 7-10).

Thermodynamic data for solid phases and many aqueous species are available in the literature. These depend strongly on an accurate calculation of the pH; our model of the H_2O-CO_2 system was developed based on ideal mixing corrected for T and P using a modified Henry's law factor and a Poynting correction, respectively (Fig. 7).
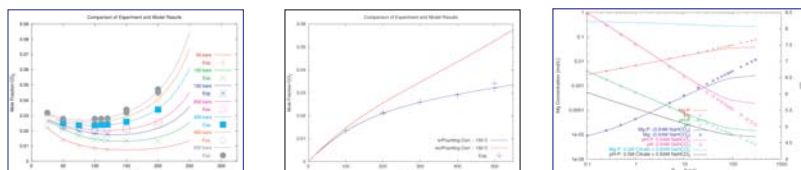

Fig. 7 Thermodynamic model of the H_2O-CO_2 system, showing comparison of modeled results with experimental data (left), effect of the Poynting correction on prediction of mole fraction CO_2, and effect of the Poynting correction on modeled activities of aqueous species. Under supercritical CO_2 conditions, omission of the Poynting correction will result in a prediction of pH that is too low.
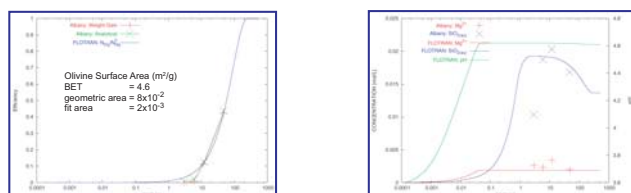

Fig. 8 Comparison of predicted evolution of fluid compositions with experimental data obtained by Albany Research Center (O'Connor et al., unpub.). Predictions were fit to experimental data for the carbonation rate (left) adjusting only the surface area. Measured surface area is significantly higher than modeled; however, modeled surface area is closer to the geometric area. Kinetic description for olivine based on Pokrovsky and Schott (2000), and magnesite obeyed local equilibrium.
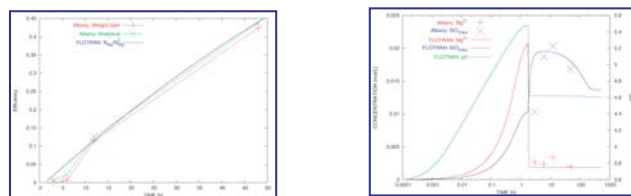

Fig. 9 Comparison of predicted evolution of fluid compositions with experimental data using the model in Fig. 8 modified with a fit value for the critical supersaturation necessary to initiate magnesite precipitation (i.e., a nucleation barrier). Fit value (log[Q/K] = 2.2) compares well with experimental values measured by Bruant et al. (2002).


Fig. 10. Scanning electron micrograph of olivine following a carbonation experiment (McKelvey et al., 2003), showing formation of a silica rind on olivine surface. Formation of such a rind may reduce reactive surface area over time, providing another possible explanation of the low fit values shown in Fig. 8.

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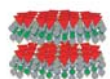
What is the rate
of serpentine dissolution?
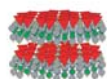
In pure water or simple salt solutions, conversion of serpentine to magnesite is limited without drastic thermal or mechanical pre-treatment, even at high partial pressures of CO_2. One limitation may be the slow rate of serpentine dissolution.

In order to evaluate this potential limitation, we have investigated the rate of dissolution of the serpentine mineral lizardite using batch and flow-through methods.
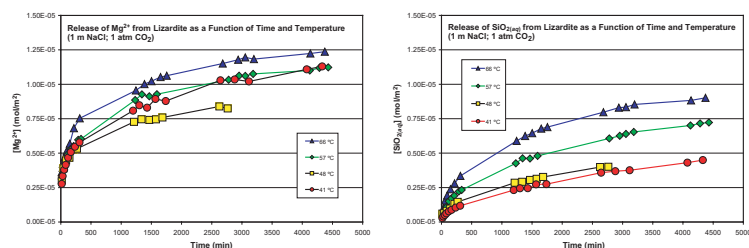

Fig. 11. Batch dissolution of lizardite (20 g in 800 ml H_2O) showing change in aqueous Mg^{2+} and SiO_2 as a function of time and temperature. The aqueous system includes 1 molal NaCl under 1 atmosphere of CO_2 yielding a pH near 5. These data were used to obtain activation energies of dissolution (Table 1) for modeling of autoclave reactions between lizardite and CO_2.

Table 1. Dissolution Parameters at 25 °C for Chrysotile/Lizardite

	$\log[k \text{ (mol/m}^2\text{/s)}]$				Ea (kJ/mol)		
	Mg	Si	pH	Solution	Mg	Si	Notes
This Study	-10.7	-10.9	5	1 m NaCl; 1 atm CO_2	-28.7	-20.6	batch; avg. value
This Study	-10.6	-10.9	5	1 m NaCl; 1 atm CO_2	-28.7	-19.3	batch; upper bound
This Study	-11.4	-11.0	5	1 m NaCl; 1 atm CO_2	-24.3	-49.1	batch; lower bound
Bales & Morgan	-11.4	-12.0	7	0.01-0.1 m salt	n.d.	n.d.	batch; constant pH
Hume & Rimstidt	-8.6	-9.4	6	dilute HCl	n.d.	n.d.	batch
This Study	-11.9	-12.1	3	dilute HCl	n.d.	n.d.	flow-through

Note: Hume and Rimstidt values corrected to 25 °C from 37 °C using the average activation energy determined in this study. Bales, R. C. and Morgan J. J. (1985) Dissolution kinetics of chrysotile at pH 7 to 10. Geochimica Cosmochimica Acta 49: 2281-2288. Hume L. A. and Rimstidt J. D. (1992) The biodurability of chrysotile asbestos. American Mineralogist 77: 1125-1128.
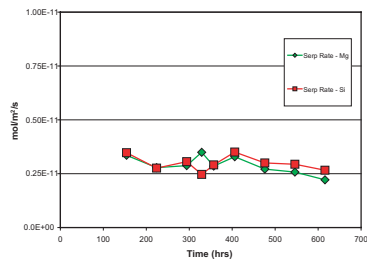

Fig. 12. Results of a flow-through experiment with lizardite. Input solution consisted of deionized water pH adjusted with HCl to pH = 3 at ambient atmosphere. Data demonstrate steady-state dissolution with respect to Mg^{2+} and $SiO_{2(aq)}$ to time up to ~500 hours. Flow-through experiments yield dissolution rates slower than suggested by batch studies (Table 1); however, solution composition differed slightly.

Enhancing the Serpentine Dissolution Rate

Fig. 13. Solution composition results for two autoclave experiments. Both were conducted at 150 °C and 2300 psi CO2. The bicarbonate experiment included 0.64 molal $NaHCO_3$ and 10^{-4} each of oxalic acid, citric acid, and EDTA with an initial pH of 8.1. The citrate experiment had 0.5 molal $Na_{2.866}$Citrate and an initial pH of 6.0. The citrate experiment produced much more Mg but neither yielded magnesite. The Na-bicarbonate experiment was initially supersaturated with amorphous silica. It is difficult to predict the saturation state of magnesite in these experiments because the stability of the citrate, oxalic, and EDTA Mg-complexes as a function of temperature are unknown.
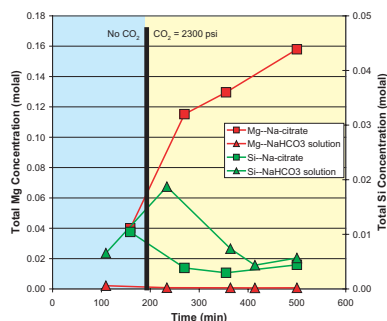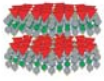
What is the rate of serpentine carbonation?
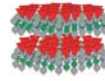
The carbonation rate for serpentine is likelyi determined by a combination of dissolution rate and precipitation rate.

Predictions of reaction paths based on our kinetic data are consistent with observed paths (Figs. 14 & 15) and indicate that magnesite precipitation may also be rate limiting (Fig. 15).
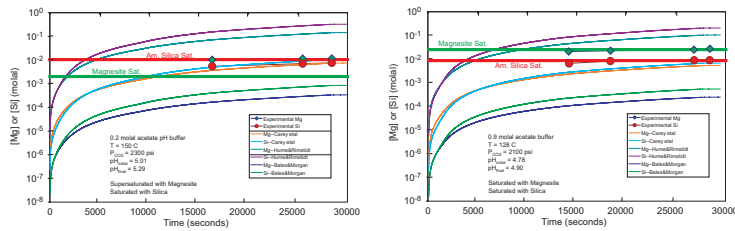

Fig. 14. Comparison of fluid-composition observed experimentally (symbols) with those predicted based on a dissolution-limited geochemical model using our batch kinetic parameters as reported in Table 1. Experimental conditions as indicated on the figures; both contained acetic acid/Na-acetate buffers. Solution compositions were extracted from the autoclave at P and T using an *in situ* filtered sampling device. Neither experiment yielded magnesite despite that both were saturated with magnesite (experiment shown on left was supersaturated with magnesite). Both achieved silica activities at or near saturation with amorphous silica. Predicted compositions based on our kinetic parameters slightly underestimate the autoclave solution compositions. However, kinetic parameters reported by Bales and Morgan (1985) and our flow-through kinetic parameters predict fluid compositions about an order of magnitude too low, whereas those reported by Hume Rimstidt (1992) predict compositions about an order of magnitude too high.
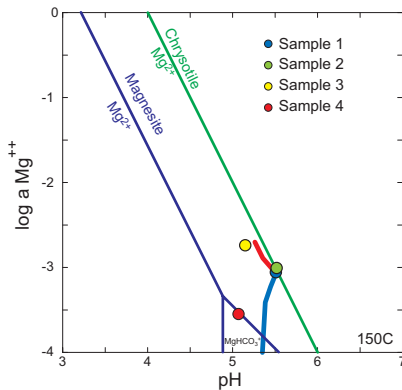

Fig. 15. Fluid speciation and mineral stabilities for the experiment depicted in Fig. 14 (left-hand figure). The first two samples were taken at 150 °C prior to application of CO_2. These samples are near or at saturation with respect to chrysotile. The third sample was taken at 2300 psi CO_2 pressure and is significantly supersaturated with respect to magnesite ($\log(Q/K) = 0.88$). We also show reaction path calculations that successfully reproduce the initial dissolution phase of the experiment (blue path) and closely model fluid composition following application of CO_2 (red path). Magnesite precipitation was suppressed in the calculations, all of which were done with Geochemist's Workbench and our

Conclusions

· Reaction of serpentine and olivine to magnesite is thermodynamically possible at moderate conditions (T < 200 °C, P < 3000 psi).

· Our data and those of Albany Research Center show that Mg-silicate can react to form magnesite at reasonable rates if the material is heat-treated to > 600 °C, mechanically ground to a semi-amorphous state, or through the use of a strong acid/strong base reaction scheme. However, these reaction methods are probably not economically feasible.

· Detailed investigations of the reaction process in serpentine demonstrate that both dissolution and nucleation may be limiting the rate of magnesite formation.

· The addition of dissolution catalysts can significantly increase the rates of dissolution, but we have not yet found a catalyst that will subsequently allow precipitation of magnesite.